First-principles Calculations of Orthorhombic to Orthorhombic Ferroelectric Phase Transition of $CdTiO_3$ and its Ferroelectric Strucuture

Hiroki MORIWAKE[1], Craig A. J. FISHER[1], Akihide KUWABARA[1], Hiroki TANIGUCHI[2], Mitsuru ITOH[2], and Isao TANAKA[1,3]

[1] Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya 456-8587, Japan

[2] Materials and Structure Laboratory, Tokyo Institute of Technology 4259 Nagatsuta, Yokohama 226-8503 Japan

[3]Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan

Perovskite titanates show ferroelectric phase transition in the low temperature region. (e.g., $BaTiO_3$, $PbTiO_3$) Among them, $CdTiO_3$ shows orthorhombic room temperature phase *Pnma*(#62), and exhibit orthorhombic to orthorhombic ferroelectric phase transition at low temperature.[1] The recent rigorous Raman scattering study has revealed an ideal classical displacive-type phase transition, in which the soft mode softens toward zero-frequency at $T_c \sim 85.5$ K obeying conventional Cochran's law.[2] However, the crystal structure in the low-temperature region is still unclear due to the rather small displacement at the phase transition and difficulty in preparation of sufficiently large and high-quality single crystals for the structural analysis.[3] Both of possible ferroelectric structures $Pna2_1$(#33) and $P2_1ma$(#26) are found depending on the samples and experimental conditions. The situation is still controversial. Lebedev[4] reported theoretical phonon calculation only Γ-point of the *Pnma* of $CdTiO_3$. He reported two softmode phonon in *Pnma* phase of $CdTiO_3$, which read to $Pna2_1$(#33) and $P2_1ma$(#26) phase. In the present study, we performed series of a first-principles calculations of $CdTiO_3$, in order to elucidate completely the mechanism of the ferroelectric phase transition and the structure of the low-temperature phase. The result clarifies that the low-temperature symmetry is $Pna2_1$ (#33) with the polarization axis along *b*-axis of the paraelectric *Pnma* phase. The calculated phonon dispersion structure clearly shows the existence of the ferroelectric soft mode in Γ-point of the *Pnma* phase, and it vanishes in the ferroelectric $Pna2_1$ phase, confirming the soft-mode-type phase transition of $CdTiO_3$.(Fig.1) However, energy gain of this ferroelectric phase transition is very tiny, its only 0.2meV/f.u. In addition, the phonon dispersion relation, in another word, soft-modes are strongly depending on the lattice volume. As shown in fig.3(a), in the tensile condition (+2% of theoretical equivalent volume), not only *B*2*u* mode which read to $Pna2_1$(#33) phase but also *B*3*u* mode which reads to $P2_1ma$(#26) phase show imaginary frequency. On the other hand, As shown in fig.3(b), in the compression condition (-2% of theoretical equivalent volume), these soft-modes are vanished. This indicates that ferroelectric phase transition of $CdTiO_3$ *Pnma* phase is very sensitive to pressure/strain. Depending on the stress/pressure both of ferroelectric phase $Pna2_1$(#33) phase and $P2_1ma$(#26) phase can be stabilized. This can be a explanation for controversial experimental results of ferroelectric structure of $CdTiO_3$. [5]

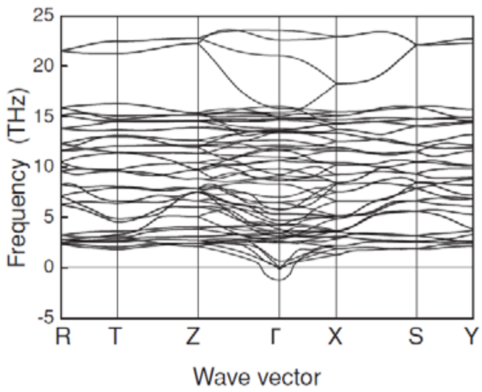

Fig. 1 Theoretical phonon dispersion curves for *Pnma* phases of $CdTiO_3$.

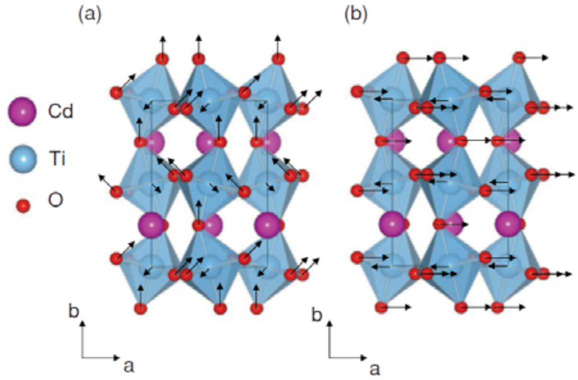

Fig. 2 Directions of ion displacements in the *Pnma* structure corresponding to (a) *B*2*u* and (b) *B*3*u* modes associated with transformations to the $Pna2_1$ and $P2_1ma$ phases, respectively.

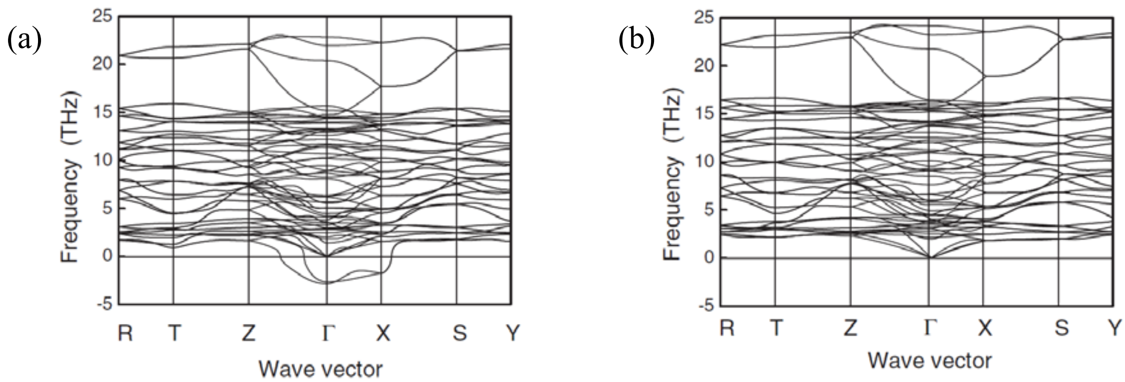

Fig. 3 Theoretical phonon dispersion curves for the *Pnma* phase of $CdTiO_3$ when the volume is uniformly (a) expanded by 2%, and (b) contracted by 2% relative to the equilibrium value.

Acknowledgements

This work was supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan through the Grants-in-Aid for Priority Area “Atomic Scale Modification” (No. 474), Scientific Research (C) No.21560708, and Green network of excellence (GRENE).

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